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PB-288 153

Arsenic Determination by the Silver Diethyldithiocarbamate Method and the Elimination of Metal Ion Interference

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Prepared for

Environmental Monitoring and Support Lab -Cincinnati, OH

Jul 78

United States
Environmental Protection
Agency

Environmental Monitoring and Support
Laboratory
Cincinnati OH 45268

EPA-600/4-78-038
July 1978

Research and Development

PB 288153

EPA

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TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/4-78-038	2.
3. RECIPIENT'S ACCESSION NO. PB288153	
4. TITLE AND SUBTITLE Arsenic Determination by the Silver Diethyldithiocarbamate Method and the Elimination of Metal Ion Interference	5. REPORT DATE July 1978 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Shingara S. Sandhu	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Claflin College Orangeburg, South Carolina 29115	10. PROGRAM ELEMENT NO. 1HD622
	11. CONTRACT/GRANT NO. R-8041640-01
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring & Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/06
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

The interference of metals with the determination of arsenic by the silver diethyldithiocarbamate (SDDC) Method was investigated. Low recoveries of arsenic are obtained when cobalt, chromium, molybdenum, nitrate, nickel or phosphate are at concentrations of 7 mg/1 or above (individually or collectively). A positive interference is obtained when the concentration of antimony is 0.3 mg/1 or above and the concentration of mercury is 1.5 mg/1 or above. Prevention of antimony and mercury interference was found to be possible by removal with an ion exchange resin. Potassium permanganate digestion at 35°C was found to be reliable.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Arsenic, water analysis, arsenic - inorganic compounds, arsenic - organic compounds metals, Distillation	Interference Digestion, ion exchange	99A

18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 38
	20. SECURITY CLASS (This page) Unclassified	22. PRICE PCA03 MFA01

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1978- 757-140/1413

EPA-600/4-78-038
July 1978

ARSENIC DETERMINATION BY THE SILVER DIETHYLDITHIOCARBAMATE METHOD AND THE ELIMINATION OF METAL ION INTERFERENCE

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.

- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

The standard methods for analysis of water and waste samples are under continual review to assure that the most accurate results possible are obtained. If a chemical interference in an important analytical procedure is discovered it must be evaluated and if necessary a procedure modification made to circumvent the interference. This report investigates the interference of metals in the analysis for total arsenic and suggests a method for removing these interferences.

Dwight G. Ballinger
Director
Environmental Monitoring and Support Laboratory

ABSTRACT

Several metal ions--chromium, cobalt, copper, mercury, molybdenum, and antimony--have been reported to interfere in the determination of arsenic in water and waste water by the Silver Diethyldithiocarbamate (SDDC) method, but the limit of interference by each ion has never been precisely evaluated. Conflicting reports have also appeared in the literature on the role of chromium and antimony as interfering ions in this method. The present study was undertaken to resolve the confusion that surrounds the use of the SDDC method for the determination of arsenic in water and waste water.

Except for minor deviations, the procedure adopted for this study is similar to the one given for the standard method. The recovery of micro amounts of arsenic in the presence of several interfering ions was studied. It was found that the SDDC method provides reliable data for arsenic concentrations in fairly polluted waters. Using this method, the recovery of arsenic up to 0.5 µg (0.01 mgL^{-1}) from polluted waters is quantitative. The absorbance peak at 410 nm is assigned to the formation of a hydrogen-SDDC complex rather than a chromium-SDDC complex. Antimony and mercury interfere with arsenic color development by yielding complexes with maximum absorbances at 510 and 425 nm respectively.

The recovery of arsenic, released on the digestion of standard solutions of natural water and cacodylic acid (sodium salt) by potassium permanganate, is found quantitative.

The research was also directed towards developing a technique to effectively concentrate and isolate arsenic from the interfering metal ions, generally found in waste water. Two different approaches were tried in order to solve the problem.

Distillation: Arsenic was quantitatively reduced to arsenic(III) by cuprous(I) chloride in hydrochloric acid and distilled as arsenic (III) trichloride before its determination by the SDDC method. The concentration of arsenic in the distillation mixture was found to be critical for the effective recovery of arsenic. The optimum recovery of arsenic seems to be at 0.0909 mgL^{-1} or at higher concentrations of arsenic. The synthetic as well as the natural water samples containing 0.01-0.05 μgL^{-1} of arsenic were concentrated to bring the arsenic concentrations within an appropriate range, but the recovery of arsenic, especially at lower concentration levels, is unsatisfactory. It appears that a major loss of arsenic takes place during the reduction of sample volume. The reduction step is also a very time-consuming and laborious

step and cannot be recommended for routine analysis of arsenic in waste water.

Ion Exchange: The synthetic and natural water samples containing arsenic were oxidized with potassium permanganate under acid conditions. The excess potassium permanganate was destroyed by the use of hydroxylamine hydrochloride. The arsenic in a water sample was isolated and concentrated by passing it through a strongly basic anion exchange (functional group-N-$(CH_3)_3$ $^+Cl^-$) column before its determination by the SDDC method. The recovery of arsenic at 0.005 mgL^{-1} is found satisfactory, with an average of 86%.

CONTENTS

Foreword..... iii
Abstract..... iv
Figures..... vii
Tables..... viii
Acknowledgment..... ix

1. Introduction..... 1
2. Conclusions..... 3
3. Recommendations..... 4
4. Materials and Methods..... 5
   Apparatus..... 5
   Materials..... 5
5. Experimental Procedures..... 6
   Ionic interference..... 6
   Elimination of ionic interference..... 6
      Distillation..... 6
      Ion exchange..... 7
6. Results and Discussion..... 8
   Ionic interference..... 8
   Ionic interference elimination..... 17
      Distillation..... 17
      Ion exchange..... 19

References..... 24

FIGURES

Number		Page
1.	Absorbance spectrum of a reagent blank recorded against a SDDC solution as reference.....	9
2.	Absorbance spectrum of a 2 μg of arsenic recorded against a SDDC solution as reference.....	9
3.	Absorbance spectrum of 2 μg of arsenic in combination with 1 mgL^{-1} each of Cr(VI), Co(II), Cu(II), Mo(VI), and Hi(II) recorded against a SDDC solution as reference.....	10
4.	Absorbance spectrum of 2 μg of arsenic recorded against a reagent blank as reference.....	10
5.	Absorbance spectrum of 2 μg of arsenic in combination with 1 mgL^{-1} each of Cr(VI), Co(II), Cu(II), Mo(VI), and Hi(II) recorded against a reagent blank as reference.....	11
6.	Effect of hydrochloric acid on the absorbance peaks at 410 nm (a) SDDC-hydrogen complex and 535 nm (b) SDDC-arsenic complex.....	11
7.	Absorbance spectrum of SDDC-mercury(II) complex.....	13

TABLES

Number		Page
1.	Recovery of Various Forms of Arsenic from Demineralized and River Water.....	15
2.	Recovery of Arsenic from Demineralized and River Water in the Presence of Interfering Ions.....	16
3.	Preliminary Arsenic Recovery by Distillation from Synthetic Aqueous Samples.....	18
4.	Arsenic Recovery by Distillation from Reduced Volume of Demineralized and River Water.....	20
5.	Arsenic Recovery by Ion Exchange from Demineralized and River Water.....	21

ACKNOWLEDGMENTS

The author is grateful to the United States Environmental Protection Agency for funding this research project. I am particularly indebted to Mr. Peter Nelson, chemist, South Carolina State College, Orangeburg, S. C., for his assistance in duplicating some of the experimental results.

I am also grateful to Dr. H. V. Manning, President; Dr. B. L. Gore, Academic Dean; and Dr. Nelson Smith, Chairman; all at Claflin College, Orangeburg, S. C., for their encouragement and cooperation in undertaking the studies reported in this bulletin.

SECTION I

INTRODUCTION

Arsenic is widely distributed in the human environment and any sample of water, if analyzed by a suitably sensitive method, will be found to contain at least a small quantity of arsenic[1]. The U.S. Public Health Service recommends that arsenic concentration in drinking water should not exceed 0.01 mg L^{-1} and that water with an arsenic concentration greater than 0.05 mg L^{-1} should be rejected for human consumption[2]. The arsenic concentration of potable water is generally less than 0.005 mg L^{-1}, although a concentration as high as 0.1 mg L^{-1} has been reported[3]. Arsenic is a suspected carcinogen[4]; consequently, there is a growing interest in arsenic contamination of the environment.

Several methods [4-13] are available for the determination of arsenic, but silver diethyldithiocarbamate(SDDC)[10] is the most widely used technique for the separation and determination of arsenic in water samples. This method consists of reducing inorganic arsenic in a water sample by acid zinc reaction to arsine (AsH_3) which is scrubbed through lead acetate impregnated glass wool and is absorbed in silver diethyldithiocarbamate dissolved in pyridine. The color developed due to arsine (AsH_3) silver diethyldithiocarbamate reaction is photometrically measured at 535 nm. Conflicting reports [12, 14] have been published on the role of chromium as an interfering ion in the standard (SDDC) method. Though chromium suppresses arsine generation[10], a color enhancement ascribed to chromium interference in the determination of arsenic by the SDDC method was observed. The authors [14] speculated that chromium SDDC-complex was responsible for the absorbance peak at 410 nm. Certain other metals--cobalt, copper, mercury, molybdenum, nickel, platinum and silver--have also been reported to interfere in the generation of arsine [10] but their limits of interference have not been thoroughly investigated. It has been indicated that the presence of antimony in a water sample interferes in the development and photometric measurement of SDDC-arsenic complex color [10] but a recent report indicates that antimony concentrations up to 0.2 mg L^{-1} do not show any significant interference.

In the early procedure [5] it was stated that antimony and mercury interfered but copper, cobalt and nickel did not interfere in the determination of arsenic which was reduced to elemental arsenic by a hypophosphate solution in hydrochloric acid. The reduced elemental arsenic was boiled for coagulation and separated by filtration and washed with water to free the filter paper of impurities. The

arsenic in the coagulum was determined by oxidation with dilute iodine solution, the excess of which was titrated with thiosulfate.

Arsenic from solution was reduced to elemental form[6] by calcium hypophosphate in hydrochloric acid. The coagulated arsenic was separated by filtering through a cotton pad and dissolved in measured quantity of standard ceric sulfate, the excess of which was titrated with standard arsenic trioxide. This procedure eliminated the interference from tin, antimony, mercury and copper.

The samples containing 1 to 100 parts per billion of arsenic were fused[7] with sodium peroxide and leached with water. The leachate was heated to coagulate cobalt, nickel and platinum which then were removed by filtration. Chromium(VI) interference was eliminated[7] by its oxidation to perchromic acid, using dilute hydrogen peroxide. The perchromic acid decomposes spontaneously to chromium(III) which does not interfere in the generation of arsine (AsH_3).

Determination of arsenic in small volume of water samples was facilitated by its distillation with cuprous chloride and hydrochloric acid[16]. The acid concentration was maintained above its azeotropic level. This not only concentrated the arsenic from water sample but also eliminated the ions that interfered in the generation of arsine and evaluation of arsenic by standard method[10].

The ion-exchange behavior of arsenic(III), at relatively high concentration (40 g L^{-1} of arsenic III), on Varion anion exchange resins was evaluated[17] in acid as well as in alkaline solutions. It was reported that about 90% of arsenic was removed from alkaline aqueous solutions. Arsenic recovery was comparatively lower in acid than in alkaline solutions.

This report presents data to resolve the confusion that surrounds the extent of ionic interference in the determination of arsenic in water and waste water by silver diethyldithiocarbamate(SDDC) method[10]. The effort has also been made to develop a methodology to eliminate the ionic interference in the generation of arsine as well as in the quantitative evaluation of total arsenic by standard method[10].

SECTION 2

CONCLUSIONS

The results of experimental studies on the recovery of micro amounts of arsenic in the presence of several interfering ions indicate that the silver diethyldithiocarbamate method provides reliable data for arsenic evaluation up to 0.01 mgL^{-1}, even in fairly polluted water. The metal ions--chromium(VI), cobalt(II), copper(II), molybdenum(VI), and nickel(II)-- up to a concentration of 5.0 mgL^{-1} do not appear to interfere in the generation of arsine. None of the metal ions in this category are responsible for an absorbance in the visible region.

Antimony(III) concentrations of 0.3 mgL^{-1} or above and mercury(II) concentrations of 1.5 mgL^{-1} or above show a significant positive interference in arsenic-SDDC color development and measurements.

The potassium permanganate digestion method is found satisfactory for the release of organically bonded arsenic before its determination by SDDC.

The distillation method is found unsatisfactory for the concentration and isolation of arsenic from interfering ions in synthetic dilute aqueous solutions and natural waters before its determination by SDDC method.

The anion exchange method reported here is found effective for eliminating the metal ions interfering in the determination of arsenic by the SDDC method, but the potential of the anion exchange technique used to separate arsenic from the interfering ions is not unlimited. The arsenic recovery decreases in the presence of extremely high anionic concentrations in polluted water, but the recovery can be improved by increasing the amount of resin used in the chromatographic column.

SECTION 3

RECOMMENDATIONS

The Silver Diethyldithiocarbamate method, in the hands of a knowledgeable and trained technician, is quantitative and can be used for routine analysis of inorganic arsenic in fairly polluted waters.

The SDDC method will not provide reliable data for waters containing total metal ion concentration of more than 5.0 mgL^{-1}.

The potassium permanganate digestion method is satisfactory for the release of organically bonded arsenic before its determination by the SDDC method.

The distillation of arsenic as arsenic(III) trichloride does not appear to provide satisfactory information for arsenic concentrations below 0.0909 mgL^{-1} in the distillation mixture.

The anion exchange technique can be effectively used for the concentration and separation of arsenic from the interfering ions found in polluted natural waters before the determination of arsenic by the SDDC method.

The anion exchange potential of the resin used in the work reported here needs further study for establishing a mathematical relation between the weight of the resin and the extent of anionic pollution of water.

SECTION 4

MATERIALS AND METHODS

APPARATUS

The arsine generator and absorber assembly have been previously described(10) and were purchased from Fisher Scientific (Cat. No. 1-405). A Beckman Model 24/25, double beam scanning spectrophotometer with 1-cm cells, equipped with a digital read out system and a strip chart recorder was used for spectra studies and absorbance measurements.

MATERIAL

The vertical condenser used during distillation of arsenic as arsenic(III) trichloride was the Allihn type, to minimize the hold up of distillate.

The ion exchange resin, Amberlite IRA-401S C.P., code 3401, was purchased from Mallinckrodt Chemical Works, St. Louis, Mo.

The stock solutions for arsenic(III), arsenic(V), chromium, cobalt, copper, mercury, molybdenum, nickel, phosphate and antimony containing 1 g L^{-1} of ionic concentration were prepared from arsenic trioxide (As_2O_3), sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), potassium chromate (K_2CrO_4), cobalt chloride ($CoCl_2 \cdot 6H_2O$), copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), mercury(II), chloride($HgCl_2$), ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), nickel nitrate ($Ni(NO_3)_2$), potassium dihydrogen phosphate (KH_2PO_4) and antimony trichloride ($SbCl_3$) respectively. The intermediate solutions were prepared by diluting the stock solutions 1:10, and working solutions containing requisite concentrations of various ions were obtained by diluting the intermediate solutions. Analytical grade reagents were used.

SECTION 5

EXPERIMENTAL PROCEDURES

IONIC INTERFERENCE

The procedure adopted for the present study is primarily similar to the one given for the standard method[10] except that a 50 ml water sample is used which requires the use of 7.5 ml of concentrated hydrochloric acid, 2.0 ml of potassium iodide and 0.5 ml of stannous chloride in hydrochloric acid. The reaction is allowed to proceed for 15 minutes at room temperature, following the addition of 3.0 g of zinc, after which the generator is transferred to a water bath at about 50°C for another 15 minutes. The solutions from the absorber tubes are poured directly into a 1-cm cell and scanned for a complete absorbance spectrum (700 nm - 350 nm), using a SDDC solution and a reagent (SDDC solution treated in the absorber tube similar to the experimental procedure but without arsenic) blank as references. Though the concentration of arsenic(III) as well as arsenic(V) in the prepared standards and river water is maintained at 2 μg or less per 50 ml of sample (.04 mg L^{-1} or less), the amount of interfering ions is varied up to 350 μg per 50 ml, (7.0 mg L^{-1}). Absorbance calibration curve using 0.0, 1.0, 2.0, 4.0 and 5.0 μg of arsenic was prepared.

ELIMINATION OF IONIC INTERFERENCE

Distillation

The distillation procedure used here has been reported[16]. The aliquots of prepared water samples containing not less than 0.01 mg of arsenic were transferred to the distillation flask which was joined to the Allihn type vertical condenser which in turn led into a distillate flask (250 ml) immersed in ice and containing 20.0 ml of dilute hydrochloric acid (1:1). The arrangement was made for the escaping hydrochloric acid vapors to be absorbed in concentrated (12 M) sodium hyroxide in a flask. The apparatus was closed to the atmosphere except for a side arm on the sodium hydroxide flask. A flexible tubing from the arm was led to a sink with running water. Two-tenths g of copper (1) chloride and enough of hydrochloric acid was added so that the water sample to acid ratio was 1:10. The volume of distillate collected varied between 45 to 55 ml. After the distillate had been collected, the apparatus was dismantled and condenser was rinsed into the distillate flash with water. The distillate was quantitatively transferred to a 100 ml volumetric flask and the volume made up to the mark with water. The aliquot volume of the distillate, containing not less than 2.0 μg of arsenic, was trans-

ferred to the arsine generator and the volume diluted to about 57.0 ml with water and hydrochloric acid in such a way that the final acid concentration in the arsine generator was about 1.6 M. The arsine was generated, color developed and measurements made according to the procedure described previously. The maximum desirable amount of arsenic in drinking water is 0.01 mg L^{-1} and the maximum safe amount is 0.05 mg L^{-1} (2) so it was found necessary that the arsenic in aqueous samples be concentrated. Consequently a 4 liters water sample in a beaker was reduced by heating on a water bath at about 50°C, to a volume so as the distillation mixture (water - acid) contained arsenic at not less than 0.0909 mg L^{-1}. The reduced sample was quantitatively transferred to four distillation flasks, (15.0 ml per flask). The beaker was washed, thoroughly, four times using 50.0 ml of concentrated hydrochloric acid per washing, which was equally divided four ways and added to the distillation flasks.

Ionic Exchange

Appropriate amount (2.0-5.0 grams) of Amberlite IRA-401S C.P., resin (depending on the extent of ions in waste water) was packed in 10.0 ml. burettes and conditioned with 100.00 ml. of 9.0 M hydrochloric acid and washed with 250.0 ml. of distilled water.

The synthetic, as well as the natural water samples, containing interfering ions and not less than 0.005 mg L^{-1} of arsenic, were digested and then eluted through the ion exchange columns. The arsenic retained by the resin was leached with 80.0 ml. of 9.0M. hydrochloric acid, followed by sufficient water to yield 100.0 ml. of effluent. An aliquot of effluent containing not less than 2.0 µg of arsenic was transferred to the arsenic generator and the volume diluted to 57.0 ml. with water, and hydrochloric acid, (if needed to maintain the acid concentration around 1.6 M). The arsenic in the effluent was determined according to the procedure described previously.

SECTION 6

RESULTS AND DISCUSSION

IONIC INTERFERENCE

Complete absorbance spectra for a reagent blank, arsenic(III), and arsenic(III) in combination with chromium(VI), cobalt(II), copper (II), molybdenum(VI) and nickel(II), each at 1.0 mg L^{-1} level (total interfering ionic concentration 5.0 mg L^{-1}), against a SDDC solution as reference, are given in Figures 1, 2 and 3 respectively. Each spectrum shows an absorbance peak around 410 nm which disappears, or is considerably reduced, Figures 4 and 5, when the same absorbance is recorded against a reagent blank.

An absorbance peak at 410 nm, similar to Figures 1, 2 and 3, is always observed no matter which one of the numerous interfering ions is used in the generator, either alone or in combination with arsenic (III), if the absorbance of the SDDC complex developed in the absorber tube is read against a SDDC solution rather than against a reagent blank. Although no mechanism for the transport of chromium from the arsine generator to the absorber, which contains SDDC reagent, was suggested, the absorbance peak at 410 nm was speculatively due to the formation of a chromium diethyldithiocarbamate complex[14]. The information presented here, Figures 1-5, does not substantiate this report, rather demonstrates that none of the interfering ions is responsible for the absorbance at 410 nm. The absorbance peak at 410 nm is observed even when the generator has nothing in it except the deionized water, hydrochloric acid and zinc. The addition of stannous chloride alone or in combination with potassium iodide does not change the nature of this absorbance peak in any way.

Accordingly, it is suggested that the absorbance at 410 nm is due to the reaction of hydrogen (generated by the acid zinc interaction) with SDDC reagent. It is further observed that the presence of arsenic in the generator, alone or in combination with the other ions, remarkably increases the peak height at 410 nm over reagent blank or interfering ions alone (Figures 1, 2 and 3). It is speculated that during the reaction of arsine (AsH_3) with SDDC, certain amount of additional atomic hydrogen becomes available for simultaneous combination with SDDC complex responsible for increased absorbance at 410 nm.

SDDC + AsH_3 ⟶ SDDC - Arsenic complex + SDDC - Hydrogen complex

The peak at 410 nm is not precisely reproducible ($\pm$30%) and is

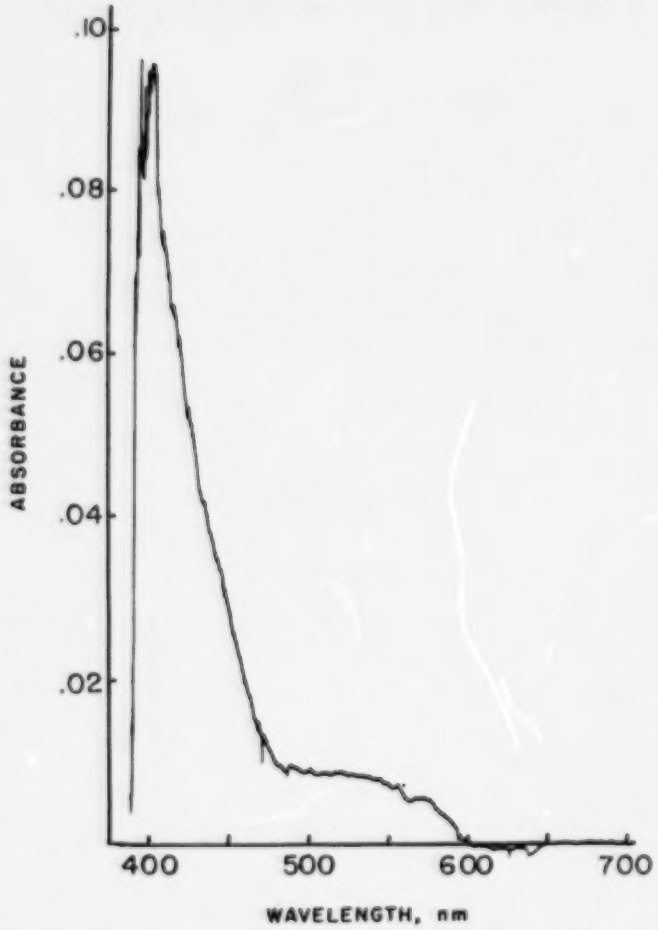

Figure 1. Absorbance spectrum of a reagent blank recorded against a SDDC solution as reference.

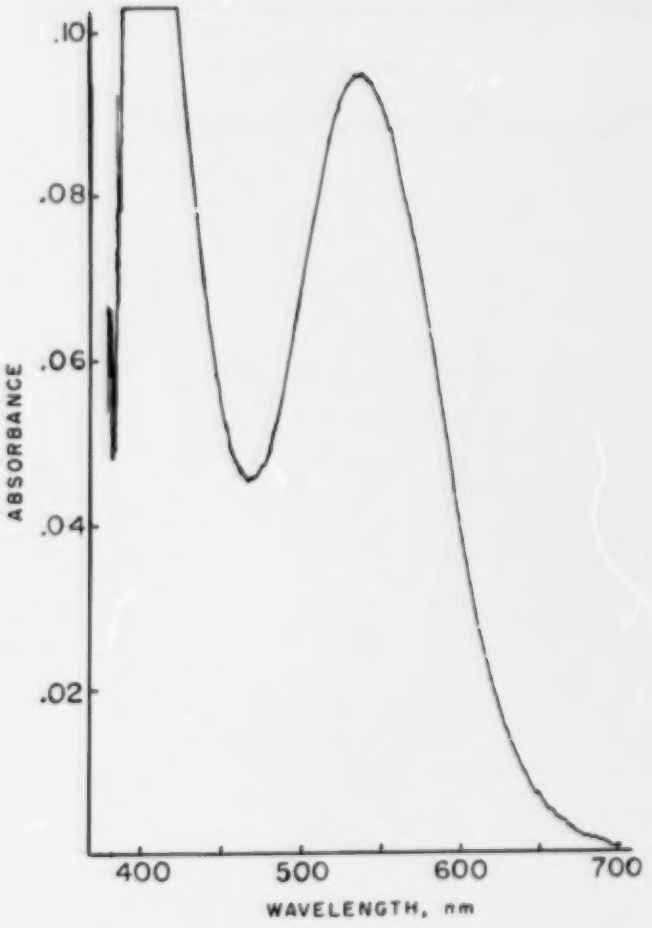

Figure 2. Absorbance spectrum of 2 μg of arsenic recorded against a SDDC solution as a reference.

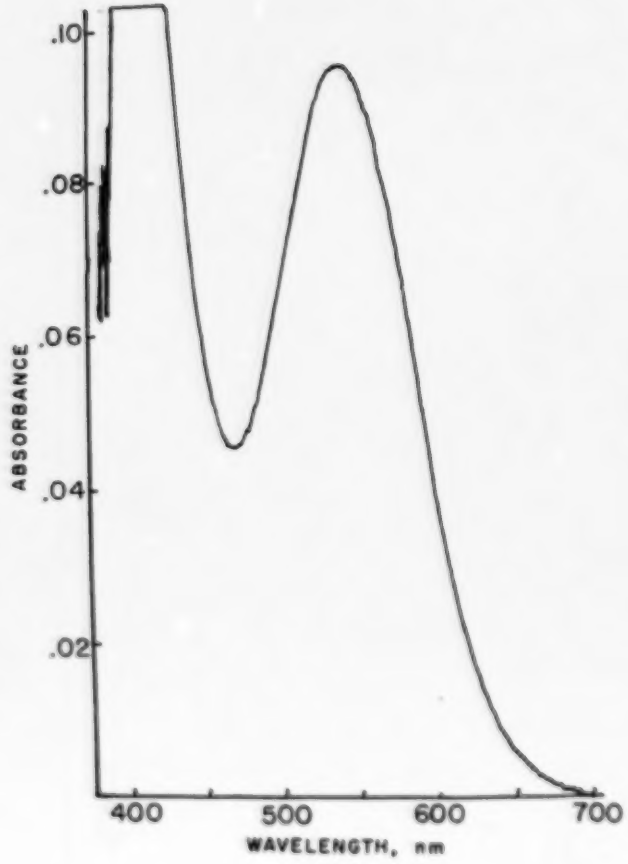

Figure 3. Absorbance spectrum of 2 ug of arsenic in combination with 1 mg L-1 each of Cr(VI), Co(II), Cu(II), Mo(VI), and Ni(II) recorded against a SDDC solution as reference.

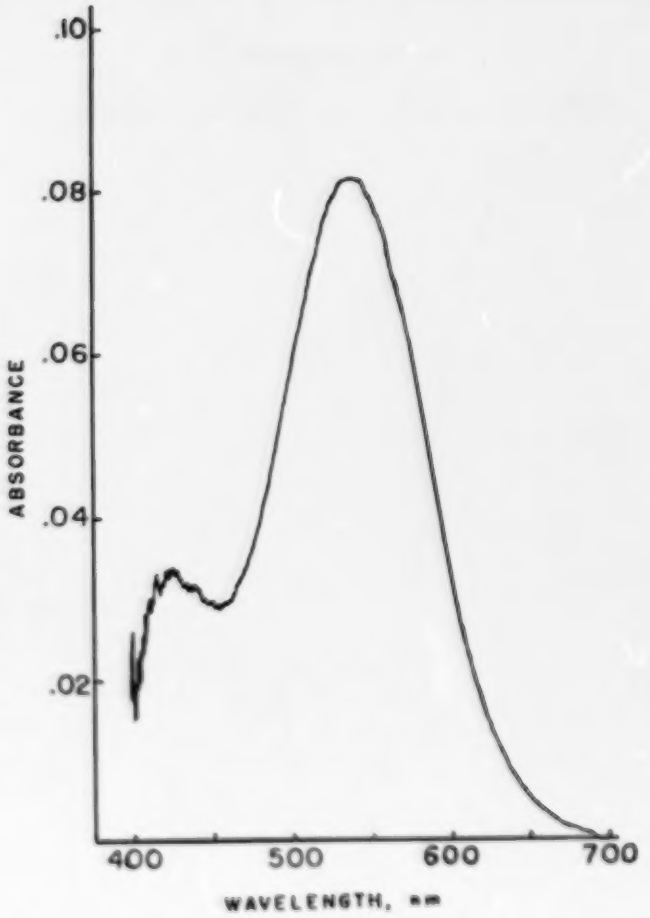

Figure 4. Absorbance spectrum of 2 µg of arsenic recorded against a reagant blank as reference.

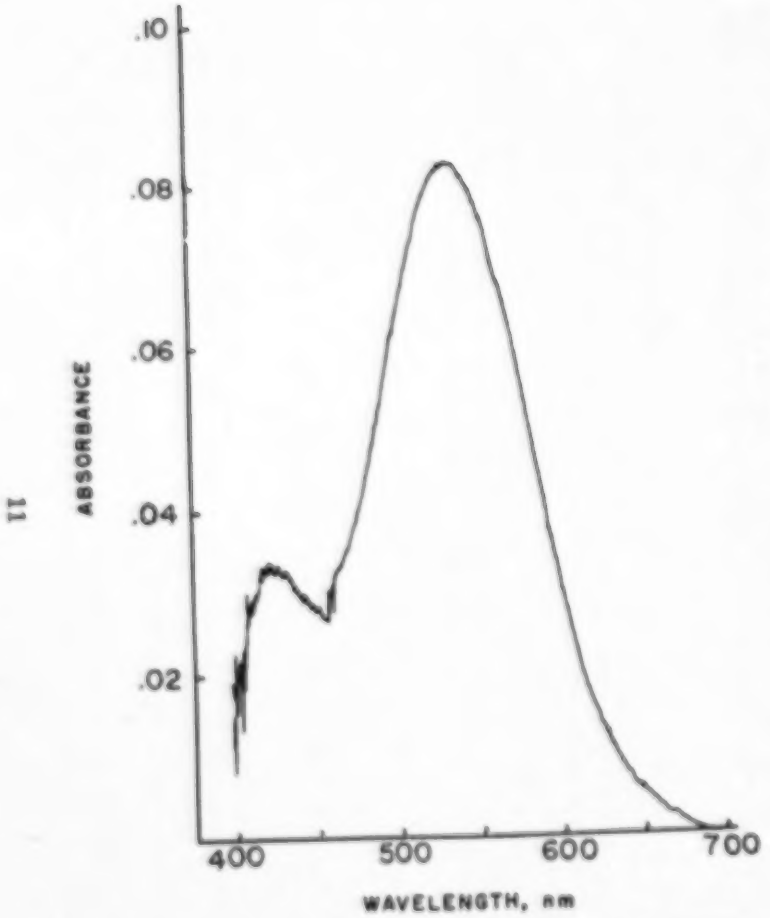

Figure 5. Absorbance spectrum of 2 µg of arsenic in combination with 1 mg L-1 each of Cr(VI), Ca(II), Cu(II), Mo(VI) and Ni(II) recorded against a reagent blank as reference.

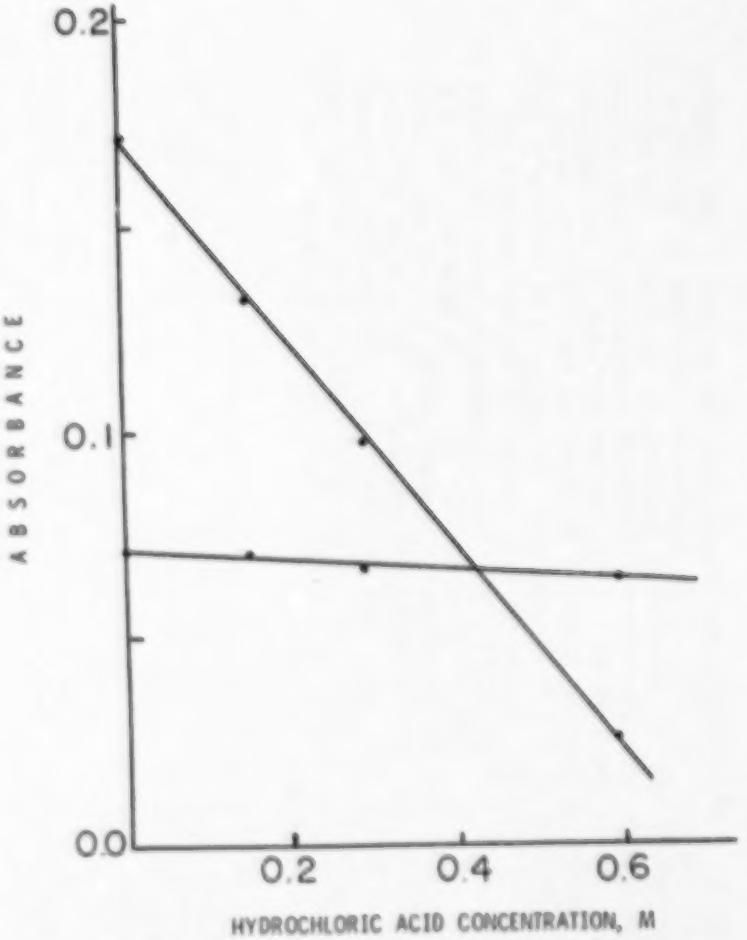

Figure 6. Effect of hydrochloric acid on the absorbance peaks at 410 nm (a) SDDC-hydrogen complex and 535 nm (b) SDDC-arsenic complex.

seen to be preferentially destroyed over the arsenic - SDDC complex peak of 535 nm. Arsenic - SDDC complex is developed as described in the procedure and the absorbance spectrum is recorded. The solution is poured back into the absorber tube and concentrated hydrochloric acid is added, one drop at a time, to the solution in the absorber tube and the absorbance spectrum is taken again. This is repeated until the peak at 410 nm disappears. Molarity of hydrochloric acid, calculated from the volume of acid added, is plotted against the absorbance at 410 nm, Figure 6. This figure also shows the effect of acid on arsenic - SDDC complex at 535 nm. It is apparent that the absorbance at 410 nm decreases in proportion to the volume of acid added, while the absorbance at 535 nm, except for a minor dilution effect, remains the same. The instability of the complex, responsible for absorbance at 410 nm, is an additional indication that hydrogen-SDDC complex rather than metal - SDDC complex is responsible for the absorbance peak at 410 nm.

The single ion absorbance spectra for Cr(VI), Co(II), Cu(II), Mo(VI) and Ni(II) are not different from the reagent blank spectrum and do not show any noticeable peak within 700 to 350 nm if the readings are taken against a reagent blank. Therefore, it appears that these ions should not show any positive interference, as suggested previously[14], in the evaluation of arsenic by the standard method. However, if the absorbance spectrum of the complex formed in the absorber tube is recorded, using an SDDC solution instead of a reagent blank as reference, a large absorbance peak at about 410 nm is noticed, which causes the elevation of the base line (Figures 1, 2 and 3), leading to an inaccurately high arsenic content (about 10%) for a given water sample.

The water samples containing 0.30 mg L^{-1} of antimony and 2.0 mg L^{-1} of mercury show absorbance peaks at 510 nm (average absorbance .007) and 425 nm (average absorbance .005) respectively and thus these ions are expected to interfere positively in the determination of arsenic by the standard method. Possible positive interference by antimony has been suggested in the past[10] but similar interference by mercury has not been reported. Ionic mercury reacts with stannous chloride in hydrochloric acid to produce metal mercury[18].

$$2Hg^{2+} + SnCl_2 + 2Cl^- \longrightarrow Hg_2^{2+} + SnCl_4$$

$$Hg_2^{2+} + SnCl_2 + 2Cl^- \longrightarrow 2Hg + SnCl_4$$

There is a distinct possibility that mercury vapors are carried over from the generator to the absorber tube containing SDDC reagent, resulting in the formation of a mercury - SDDC complex, responsible for an absorbance peak at 425 nm (Figure 7).

The amount of arsenic recovered from demineralized water is quantitative up to an arsenic concentration of 0.5 μg or .01 mg L^{-1}

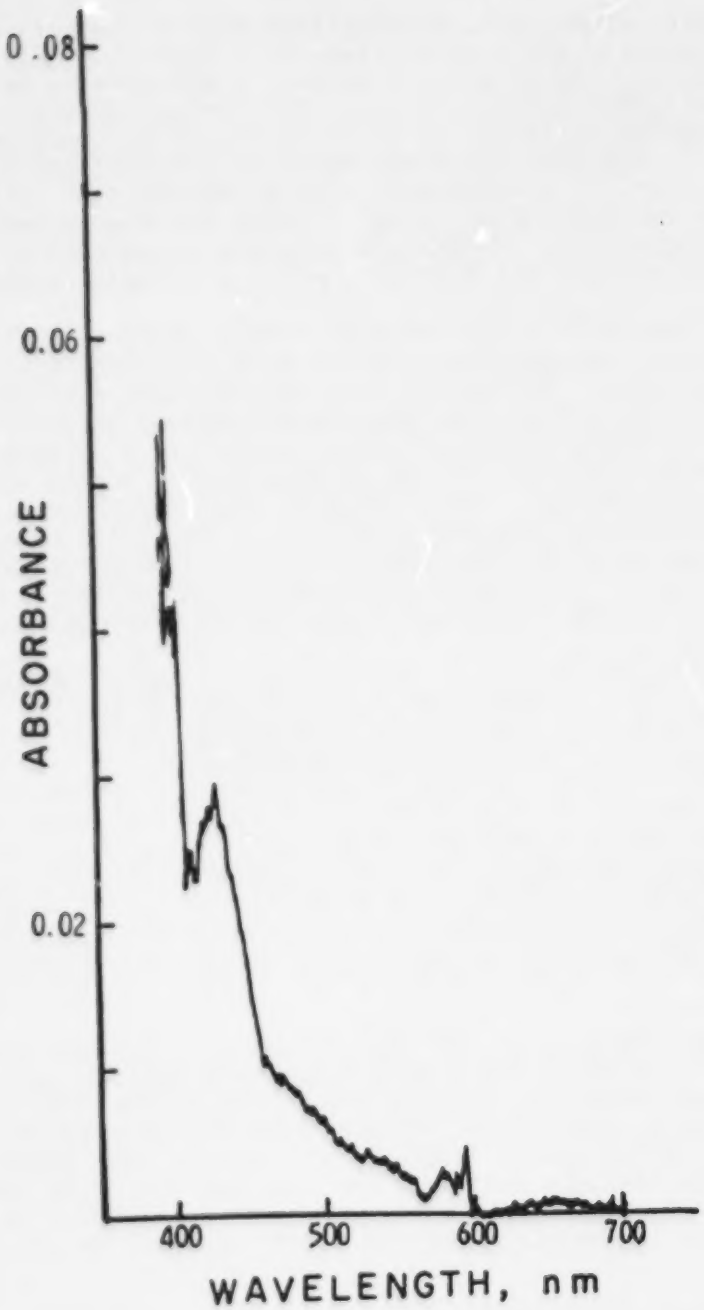

Figure 7. Absorbance spectrum of mercury recorded against a reagent blank.

(Table 1). Arsenic recovery from demineralized water in the presence of various interfering single ions is presented in Table 2. This information suggests that the recovery of arsenic is not affected in the presence of chromium(VI), cobalt(II), copper(II), molybdenum(VI), nickel(II), nitrate and phosphate, up to an individual ion concentration of 5.0 mg L^{-1}. But when the single metal ion concentration is increased beyond 5.0 mg L^{-1}, a decrease in arsenic recovery from the standard solutions is observed and at 7.0 mg L^{-1} level the arsenic recovery decreases approximately 10%. Nitrate and phosphate concentrations up to 100.0 mg L^{-1} do not show any observable effect on arsenic recovery.

It has been reported[12] that antimony concentrations up to 0.2 mg L^{-1} did not produce any observable interference in determining arsenic by the SDDC method. The present study suggests that antimony concentration of 0.2 mg L^{-1} does not show any significant change in the recovery of arsenic from standard solutions; however, when antimony concentration is raised to 0.3 mg L^{-1}, the apparent rate of arsenic recovery increases by about 10 percent. The location of arsenic absorbance peak shifts toward 510 nm in the presence of antimony. This shift seems proportional to the amount of antimony present in a solution containing 0.04 mg L^{-1} of arsenic. The mercury concentrations at 1.5 mg L^{-1} and above show a significant positive interference in the recovery of arsenic.

Interference by several ions in combination was studied by preparing standard solutions, containing 0.04 mg L^{-1} of arsenic and varying the concentrations of each ion, chromium(VI), cobalt(II), copper(II), molybdenum(VI), nickel(II), phosphate and nitrate, up to 1.0 mg L^{-1}. The results on the recovery of arsenic in the presence of a combination of ions are also given in Table 2. There is no significant interference by these metal ions up to a combined concentration of 5.6 mg L^{-1} (0.8 mg L^{-1} each ion) but when the combined concentration is increased above this level there is an observable decrease in the recovery of arsenic from demineralized water. A combined concentration of 7.0 mg L^{-1} (1.0 mg L^{-1} each ion) decreases the arsenic recovery from standard solutions by about 10%.

A combined concentration of two ions, chromium(VI) and cobalt(II), each at 3.5 mg L^{-1}, decreases the arsenic recovery by about 10 percent. A molybdenum(VI) and copper(II) combination, as well as the combination of any other two metal ions in this category at a total concentration of 7.0 mg L^{-1}, show similar results (Table 2). It appears that, under the present set of experimental conditions, the ionic specificity of the elements that interfere in arsine generation is not as important as their total concentration in inhibiting the recovery of arsenic from the standard solutions.

The studies are also carried out using natural water from the Edisto River, Orangeburg, S. C., which was spiked with arsenic as well as with interfering ions. Because only inorganic arsenic is reduced to arsine[10] a digestion step, as suggested in the literature, using nitric and sulfric acids[12] was tried for the release of organically bonded arsenic.

TABLE 1. RECOVERY OF VARIOUS FORMS OF ARSENIC FROM DEMINERALIZED AND RIVER WATERS

Concentration mg L^{-1}						
	Demineralized water			River water		
Theoretical	Determined[1]	Recovery %	Standard deviation %	Determined[2]	Recovery %	Standard deviation %
			As(III)			
0.01	.0102	102	5.7	---	---	---
0.02	.0196	98	4.3	0.0214	107	5.6
0.04	.0410	102	3.4	0.043	108	4.5
			As(V)			
0.01	0.0100	100	5.8	---	---	---
0.02	0.0208	104	4.9	---	---	---
0.04	0.0395	99	4.0	---	---	---
			As(III) + As(V) (50:50)			
0.01	0.0095	95	5.6	---	---	---
0.02	0.0201	100	3.1	---	---	---
0.04	0.0405	101	3.5	0.044	109	5.8

1 Mean of 35 determinations

2 Mean of 20 determinations

TABLE 2. RECOVERY OF ARSENIC FROM DEMINERALIZED AND RIVER WATER IN THE PRESENCE OF INTERFERING IONS

		Concentration mg L^{-1}			
		Demineralized water		River water	
Ions[1] added	Theoretical	Recovery[2] %	Standard deviation %	Recovery[3] %	Standard deviation %
Individually					
5	0.02	99.6	5.9	107	6.6
5	0.04	98.9	5.7	108	6.5
7	0.04	89.5	4.3	97	8.3
Sb					
0.2	0.04	99.6	4.7		
0.3	0.04	109.3	4.9		
Hg					
1.5	0.04	107.5	4.5		
5.0	0.04	134.2	4.4		
Collectively[1]					
5.6, 0.8 each	0.04	96.2	4.7	103.3	7.2
7.0, 1.0 each	0.04	89.4	4.0	97.1	9.3
Cr(VI) + Co(II)					
3.5 each	0.04	88.2	3.5		
Mo(VI)* + Cu(II)					
3.5 each	0.04	90.2	4.2		

1 Ions used Co(II), Cr(VI), Cu(II), Mo(VI), NO_3^-, Ni(II) and PO_4^{-3}

2 Mean of 12 determinations for each system

3 Mean of 6 determinations for each system

* Results for other combinations, not reported here

Data on the recovery of arsenic using this digestion method are acceptable for standard solutions but the recovery of arsenic, added to the river water, is inconsistent and reproducibility is very poor. Consequently, potassium permanganate method[19] with minor modification is adopted for the digestion of water samples. One-tenth ml of 5.0% potassium permanganate followed by 5.0 ml of concentrated sulfuric and 0.3 ml of nitric adic is added to 50 ml of water sample, containing at least 1 μg of arsenic. The water sample is placed in a water bath for an hour at 35°C and the excess of potassium permanganate is destroyed by adding 1.5% hydroxylamine hydrochloride. Hydroxylamine hydrochloride is added a drop at a time to avoid its excess in the generator. The reliability of the potassium permanganate method was further investigated using known concentrations (2 μg and 1 μg of arsenic per 50 ml) of dimethylarsenic acid (cacodylic acid, sodium salt). This method not only gives an acceptable recovery and reproducibility for arsenic in natural water as well as in organoarsenicals (88.8% arsenic recovery from cacodylic acid), but is less laborious than the acid digestion method previously used[12]. The recovery of arsenic from the river water is greater than the amount added (Tables 1 and 2). The difference approximately equals the amount of arsenic found in the Edisto River.

IONIC INTEREFERENCE ELIMINATION

Distillation

It has been suggested in the literature[20] that trivalent arsenic can be quantitatively removed as chloride from an aqueous solution containing hydrochloric acid corresponding to the azeotropic or constant boiling mixture at 110°C. With the exception of germanium, no other element distills under these conditions. Various workers[16, 21, 22] have attempted to apply this technique for the concentration of arsenic from aqueous solutions before its determination by standard method[10]. Distillation was regarded as a process[16] in which the percentage of arsenic recovered from aqueous solutions depends on the sample volume (V), the amount (micrograms) of arsenic present in the solution and amount of hydrochloric acid and copper(I) chloride used. Some of these variables were studied[16] but the role of changing sample volume (V) at various arsenic concentrations was not investigated. The distillation system was not tried for the determination of arsenic at levels contained in drinking water supplies or surface water samples.

The recovery of arsenic at different concentration levels is shown in Table 3. The arsenic recovery decreases sharply as the concentration of arsenic in the distillation mixture decreases beyond 0.0909 mg L^{-1}. It appears that the concentration of arsenic rather than its total amount in the distillation mixture plays a critical role in determining the efficiency of the distillation process. The lower limit of arsenic in distillation mixture for its maximum recovery seems to be around 0.0909 mg L^{-1}. Consequently, the distillation process would not be very effective for the determination of arsenic at levels in drinking water unless the sample volume is reduced to bring the arsenic concentration within

TABLE 3. PRELIMINARY ARSENIC RECOVERY BY DISTILLATION FROM SYNTHETIC AQUEOUS SAMPLES

Sample vol. ml	Arsenic in sample mg x 10^{-3}	Acid added ml	Arsenic concentration in distillation mixture mg L^{-1}	Arsenic* Recovery %	Standard deviation %
15.0	10.0	150.0	0.0606	90.7	6.6
30.0	10.0	300.0	0.0303	80.0	10.0
50.0	10.0	500.0	0.0182	56.0	20.0
15.0	15.0	150.0	0.0909	94.2	6.0
30.0	15.0	300.0	0.0455	86.0	10.6
50.0	15.0	500.0	0.0273	78.0	12.7
15.0	50.0	150.0	0.3030	100.5	3.6
30.0	50.0	300.0	0.1515	99.6	4.3
50.0	50.0	500.0	0.0909	96.0	4.8

Volume of distillate collected 45-55 ml

Amount of copper (I) chloride used 0.2 grams per distillation

* Mean of 15 determinations

* Readings corrected for reagent arsenic, based on the label values

the range of its optimum recovery. For the same reason, bubbling of hydrochloric acid gas into a one liter water sample[16] until the hydrochlorice acid concentration reaches the desired level does not seem to be practical.

The recovery of arsenic from the synthetic as well as the aqueous samples drawn from the Edisto River, Orangeburg, S. C., is not uniform (Table 4). These samples were concentrated to bring the arsenic concentration within the range of its maximum recovery (0.0909 mg L^{-1}). The natural water samples from the Edisto River were spiked with arsenic as well as with interfering ions (1.0 mg L^{-1}) each of Co(II), Cr(VI), Cu (II), Hg(II), Mo(VI), Ni(II), and Sb(III), and digested, using potassium permanganate, before they were subjected to the volume reduction step. It is speculated that this concentration step is responsible for the loss of arsenic and thus results in its low recovery. The loss of arsenic appears to be about the same irrespective of the original amount of arsenic in a liter of aqueous sample. The recovery of arsenic from the river water is given in Table 4.

Ion Exchange

The resin used in the present study is in the basic anion form with $-N-(CH_3)_3^+ Cl^-$ as the functional group and is effective in separating the anions from the cations. Hydroxylamine hydrochloride used to destroy the excess of potassium permanganate during the digestion of aqueous samples also reduces the chromate (CrO_4^-) and dichromate ($Cr_2O_7^-$) to cationic form of chromium (Cr^{3+}). Excess hydroxylamine hydrochloride was carefully avoided.

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O \qquad (E^o = 1.5IV)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2\,Cr^{3+} + 7H_2O \qquad (E^o = 1.33V)$$

$$CrO_4^{2-} + 8H^+ + 3e \longrightarrow Cr^{3+} + 4H_2O \qquad (E^o = 1.19V)$$

$$AsO_4^{3-} + 2H^+ + 2e \longrightarrow AsO_3^{3-} + H_2O \qquad (E^o = 0.56V)$$

$$2NH_3OH^+ \longrightarrow N_2 + 4H^+ + 2H_2O + 2e \qquad (E^o = 1.87V)$$

$$N_2 + H_2O \longrightarrow N_2O + 2H^+ + e \qquad (E^o = 1.77V)$$

Even if the part of arsenate (AsO_4^-) may have been reduced to arsenite (AsO_3^-) it still remains in the anionic form. The amount of resin used for preparing ion exchange columns depends on the extent of impurities expected for removal from the aqueous samples. Generally, higher amounts of impurities require more resin.

The results on the recovery of arsenic by ion exchange method is shown in Table 5. It appears that arsenic in water samples can be quantitatively concentrated by use of ion exchange before its determi-

TABLE 4. ARSENIC RECOVERY BY DISTILLATION FROM REDUCED AQUEOUS SAMPLE VOLUME OF DEMINERALIZED AND RIVER WATER

Concentration mg L^{-1}				
	Demineralized water		River water	
Theoretical	Recovery* %	Standard deviation %	Recovery*[1] %	Standard deviation %
0.010	78.2	10.7	70.8	12.2
0.015	80.5	9.0	72.0	13.4
0.020	79.0	10.8	71.8	13.5
0.05	86.0	8.6	80.0	11.6

* Mean of 20 determinations

1 Readings corrected for arsenic in river water (0.07 mg L^{-1})

* Readings corrected for reagent arsenic, based on label values

TABLE 5. ARSENIC RECOVERY BY ION EXCHANGE FROM DEMINERALIZED AND RIVER WATER

Interfering ions added	Theoretical	Concentration mg L^{-1} Demineralized water Recovery[1] %	Demineralized water Standard deviation %	River water Recovery[2] %	River water Standard deviation %
		Resin used, 2.0 grams			
0	0.020	96.7	4.6		
0	0.010	92.0	5.0	86.0	5.4
0	0.005	88.6	5.8		
Individually[3]					
10.0	0.005	87.0	6.0		
Sb					
1.0	0.005	88.3	5.8		
Hg					
5.0	0.005	88.4	5.8		
Collectively[4]					
9.0 (1.5 each)	0.005	86.8	6.3		
18.0 (3.0 each)	0.005	67.8	7.8		
		Resin used, 5.0 grams			

(continued)

TABLE 5. (continued)

Interfering ions added	Theoretical	Demineralized water Recovery[1] %	Standard deviation %	River water Recovery[2] %	Standard deviation %
18.0 (3.0 each)	0.005	81.0	7.5		

[1] Mean of 12 determinations, readings corrected for reagent arsenic based on label values

[2] Mean of 8 determinations, readings corrected for river water and reagent arsenic

[3] Ions used Co(II), Cr(VI), and Ni(II)

[4] Ions used Co(II), Cr(VI); Cu(II), Hg(II), Ni(II) and Sb(III)

nation by the standard method[10]. The maximum desirable amount of arsenic in drinking water is 0.01 mg L^{-1} and the maximum safe amount is 0.05 mg L^{-1} [2]. The ion exchange method used here can be effectively applied for the concentration of arsenic from drinking water even below the desirable limit to facilitate its determination by the standard method[10].

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